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Direct Synthesis and Bonding Properties of the First μ^2-η^2,η^2-Allyl-Bridged Diiridium Complex

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Supporting Information

ABSTRACT: The direct synthesis of the first μ^2-η^2,η^2-allyl-bridged diiridium complex ($[2]^+$), bearing the uncommon counterion $[IrCl_2(COD)]^-$ ($[3]^-$), is described. Both bridging moieties in $[2]^+$, namely, allyl and acetate, are introduced in a single reaction step from $[\{IrCl(COD)\}_2]$ (**1**) and allyl acetate. A combination of X-ray crystallography and density functional theory calculations reveals pronounced metal–allyl π-back-bonding.

Prior to the mid-20th century, coordination chemistry was mainly shaped by Alfred Werner's (1866–1919) work on single metal (M) ions surrounded by defined ligand spheres.[1] It was not until the early 1960s that a novel concept in the field, namely, multicenter chemistry by means of M–M bonding, was introduced.[2] After the initial reports, which led to heated debates, a common consensus on the existence of these bonding interactions was reached. Ultimately, extensive research in the field over the past 50 years has yielded a plethora of structural motifs and applications, particularly of d-block elements from groups 5–10.[2] Within group 9, the chemistry of M–M-bonded rhodium complexes is fairly established, while the respective cobalt and iridium compounds still remain relatively rare (L_4MML_4 and L_5MML_5 motifs with d^7–d^7 configurations).[2,3] This might appear surprising, given the fact that the related, isoelectronic compounds within a group are in general synthetically accessible. For the synthesis of these structures, bridging ligands can be beneficial, with a prominent example being the allyl ligand (Figure 1).[4]

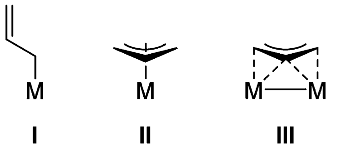
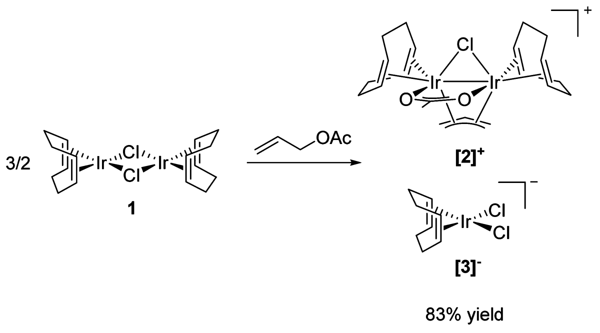


Figure 1. Allyl ligand binding modes.

While the most common coordination modes are of types **I** and **II**, i.e., η^1/σ and η^3/π coordination to a single metal center, μ^2 bridging (**III**) of dinuclear complexes bearing M–M bonding interactions is almost exclusively limited to elements of groups 6, 8, and 10.[5] This work reports the direct synthesis of the first μ^2-η^2,η^2-allyl-bridged diiridium compound bearing an anionic iridium complex as the counterion. Besides characterization by X-ray crystallography, NMR, IR, UV–vis, emission spectroscopy, and CV measurements, density functional theory (DFT) calculations were used to gain insight into M–M and M–ligand bonding.

Complex $[2][3]$ consists of the cationic μ^2-η^2,η^2-allyl-bridged diiridium fragment $[2]^+$ and $[IrCl_2(COD)]^-$ ($[3]^-$) as the counteranion (Scheme 1). It was obtained via the direct reaction of $[\{IrCl(COD)\}_2]$ (**1**) and allyl acetate in 83% yield after crystallization. The oxidative addition of the allyl compound to the iridium(I) dimer results in the introduction of two bridging ligands in one reaction step upon C–O bond cleavage to form the cationic M–M-bonded iridium(II)–iridium(II) complex $[2]^+$. The counteranion $[3]^-$ has rarely been reported,[6] and usually several reaction steps are necessary to access structures bearing multiple bridging ligands.[2,5] In an analogous attempt, $[\{RhCl(COD)\}_2]$ was employed; however, no reaction occurred, and only the starting material could be retrieved.

Scheme 1. Synthesis of Compound $[2][3]$



Single crystals suitable for X-ray diffraction were obtained by layering a solution of $[2][3]$ in dichloromethane with *n*-pentane (Figure 2). While the crystallographic data of $[3]^-$ correspond to the existing data,[6] to the best of our knowledge, cationic iridium dimer $[2]^+$ is the first example of a symmetrically allyl-bridged diiridium complex. In addition, the number of acetate-bridged diiridium compounds is also very limited.[7] Only one example of an allyl- and acetate-bridged M–M complex, in this case a dipalladium compound, has been reported to date.[5a,b]

Aside from some minor distortions, cation $[2]^+$ displays C_s symmetry. The Ir1⋯Ir2 distance of 2.8736(3) Å is fairly long compared to the common M–M distance between 2.5 and 2.7

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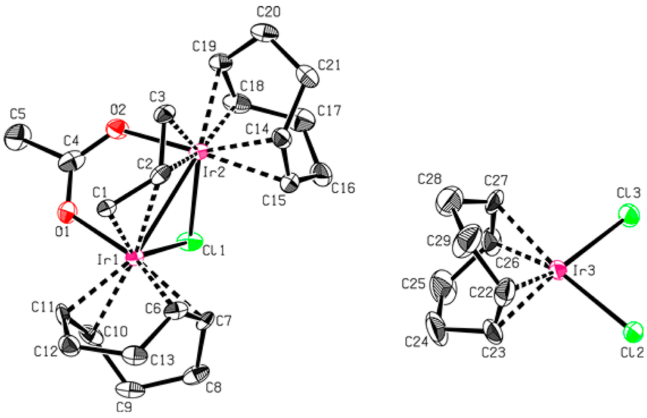

Figure 2. ORTEP style view of [**2**][**3**] with thermal ellipsoids shown at a 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Ir1−Ir2 2.8736(3), Ir1−C1 2.105(6), Ir1−C2 2.489(5), Ir2−C3 2.111(6), Ir2−C2 2.454(6), C1−C2 1.441(8), C2−C3 1.454(7).

Å.[2] However, there are examples for diiridium compounds with similar values, which suggest the existence of M−M bonding interactions.[8] Regarding the Ir−Cl bond lengths, a slight elongation can be observed from 2.399(5) and 2.400(5) Å to 2.4558(14) and 2.4669(13) Å, respectively, compared to those in **1**.[9] The Ir1−Cl1−Ir2 bond angle of 71.43(4)° is compressed relative to 74.5(1)/74.7(1)° in the starting complex, while the average Ir···C_{COD} distances are prolonged from 2.09 to 2.15 Å (trans to the Ir−Ir bond) and 2.19 Å (trans to acetate). For the acetate ligand, the Ir1−O1 bond length of 2.082(4) Å and the Ir2−O2 bond length of 2.083(4) Å correspond to reported values.[7] Similar to the bridging acetate ligand, the allyl ligand is almost symmetrically disposed about both iridium centers with Ir1···C1/Ir1···C2 and Ir2···C3/Ir2···C2 distances of 2.105(6)/2.489(5) Å and 2.111(6)/2.454(6) Å, respectively, suggesting η^2 coordination to both metal centers.[10] Notably, the Ir−$C_{methylene}$ bond lengths are among the shortest for any Ir−C_{allyl} bond reported so far, while the bond lengths in the allyl ligand of 1.441(8) Å for C1−C2 and 1.454(7) Å for C2−C3 are elongated compared to the average bond length of 1.41 Å.[11] The prolonged Ir−Ir and C−C_{allyl} bonds in combination with short Ir−C_{allyl} bonds indicate pronounced M−allyl π-back-bonding.

In order to gain further insights into the bonding properties of [**2**][**3**], DFT calculations were performed at the B3LYP/6-311++G** level of theory with good agreement of the experimental and computed structural data (Table S1 in the Supporting Information, SI), similar to a report on dimolybdenum compounds.[5c] A frontier molecular orbital analysis of [**2**]$^+$ is shown in Figure 3 (for [**3**]$^-$, see Figure S7 in the SI). In the lowest unoccupied molecular orbital (LUMO), the $d_{x^2-y^2}$ orbitals of the diiridium unit interact in an antibonding (σ^*) fashion. The same is observed for interaction of the M−M unit and the nonbonding π-allyl ligand orbitals. For the highest occupied molecular orbital (HOMO), both M−M interaction and the interplay with the allyl ligand are of σ-binding nature. However, as can be seen in the orbital representation (Figure 3, bottom), there is significant back-bonding from the M−M σ-bonding orbital into the π^* orbitals of the allyl ligand. The population of the antibonding ligand orbitals leads to a weakening and elongation of both the C−C and M−M bonds and to stronger Ir−ligand bonding. All of these features are reflected in the crystallographic data (vide supra).

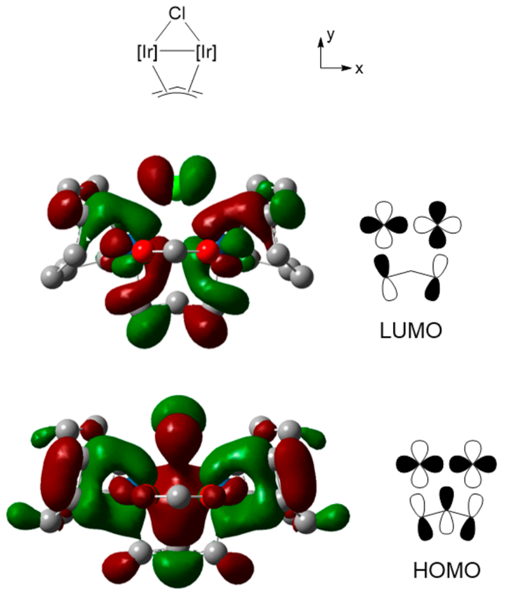

Figure 3. Illustration of perspective (top) as well as LUMO (middle) and HOMO (bottom) representations of [**2**]$^+$ including a depiction of the contributing orbitals as obtained from DFT calculations (for further details, see Figure S8 in the SI).

Considering ^{1}H NMR spectroscopy, it seems worth noting that the allyl methylene protons show highly diastereotopic resonances with a chemical shift difference of more than 3 ppm, most probably caused by C−H···O hydrogen bonding to the acetate ligand (Figure S12 in the SI).[12] The computed IR absorption patterns of [**2**]$^+$ and [**3**]$^-$ correspond well to the experimental solid-state IR spectrum of the title compound, supporting the accuracy of the calculated data (Figure S9 in the SI). The relative positions of the symmetric and asymmetric carboxylate absorption bands $\tilde{\nu}_{sym}$ and $\tilde{\nu}_{asym}$ at 1553 and 1445 cm^{-1} illustrate the bridging μ^2-coordination mode of the acetate ligand.[13] [**2**][**3**] exhibits two strong absorption bands at 228 and 260 nm in the UV−vis spectrum, while emission spectroscopy reveals that the associated excited states may relax into photoluminescent states with corresponding emission bands at 437 and 473 nm (λ_{Stokes} = 209 nm; Figure S10 in the SI). In cyclic voltammetry experiments, multiple redox processes were observed because of the number of redox active sites in [**2**][**3**], all of which appear to be irreversible ($E_{1/2}$ = −2.10, −0.20, and +0.36 V vs Fc/Fc$^+$; Figure S11 in the SI). This is in accordance with a report on the electrochemical behavior of an iridium(I) complex with [**3**]$^-$ as the counterion.[6a]

In summary, the direct synthesis of the first symmetrically allyl-bridged diiridium complex ([**2**][**3**]) has been achieved. Besides high yield (83%) and the introduction of two bridging moieties in a single reaction step, the title compound bears the uncommon counterion [**3**]$^-$. Detailed characterization, especially the combination of X-ray crystallography and DFT calculations, reveals pronounced M−ligand back-bonding. This is evidenced by a long Ir−Ir bond [2.8736(3) Å], elongated C−C_{allyl} bonds [1.441(8)/1.454(7) Å], and exceptionally short Ir−$C_{methylene}$ bonds to the allyl ligand [2.105(6)/2.111(6) Å] and is further underpinned by a computational frontier molecular orbital analysis. Current work is focused on the synthesis and characterization of similar allyl-bridged compounds bearing other d-block elements, which will enable a systematic comparison of the structural and electronic properties, starting within group 9.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental and computational details, spectroscopic and electrochemical data, and X-ray crystallographic data in CIF format. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00671. CCDC 1053700 contains crystallographic data and can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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(11) According to a comprehensive search in the CCDC database. Average bond lengths: $\mathrm{Ir{-}C}_{\text{methylene-}\eta^1\text{-allyl}}$ 2.15 Å, $\mathrm{Ir{-}C}_{\text{methylene-}\eta^3\text{-allyl}}$ 2.21 Å, $\mathrm{Ir{-}C}_{\text{methine-}\eta^3\text{-allyl}}$ 2.16 Å; $\mathrm{C{-}C}_{\text{allyl}}$ in μ^2-η^2,η^2-allyl-bridged dimetal complexes 1.41 Å.

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